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ULTRAVIOLET ABSORPTION SPECTRA OF SOLUTIONS OF BROMOTOLUENES IN ISOBUTYL ALCOHOL AT DIFFERENT TEMPERATURES*

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ABSTRACT. Ultraviolet absorption spectra of 0.2% and 40% solutions of ortho-, meta- and para-bromotoluene in isobutyl alcohol in the liquid state and in the solid state at −180°C have been investigated and the results have been compared with those obtained in the case of pure substances in different states, as reported by previous workers. The splitting of the absorption bands in the case of ortho- and meta-bromotoluene in the solid state observed by previous workers is found to be absent in the case of 0.2% frozen solution, but the spectrum due to 40% frozen solution in each case shows broad band system which seems to be composed of two systems of bands, one due to 0.2% frozen solution and another due to the pure substance in the solid state. The absorption spectrum of 0.2% solution of para-bromotoluene resembles that due to the vapour and that due to 40% solution resembles that due to the pure liquid. The absorption spectra of frozen solutions of the para compound do not show any splitting as in the case of pure crystals. It has been concluded that splitting of the absorption band is not due to lattice field but may be due to the presence of strongly assymetric groups of molecules in the crystals.

INTRODUCTION

The ultraviolet absorption spectra of the solutions of ortho-, meta- and para-chlorotoluene in isobutyl alcohol in the liquid state and in the solid state at −180°C were investigated recently (Roy, 1956) in order to find out the influence of environments on the nature of absorption spectrum of the molecule in the solid state at −180°C. In the case of the pure ortho-and meta compounds in the solid state at −180°C, Swamy (1952) observed splitting of the band systems, while in the case of the solution in the solid state no such splitting was observed (Roy, 1956). It was concluded that when the molecules are surrounded by similar mblecules in the solid state the influence of the intermolecular field is largest, because owing to presence of permanent electric moment the molecules become strongly associated with each other through virtual linkages and such association causes splitting of the energy level. But in the case of the frozen solutions of ortho- and meta-chlorotoluene the molecules are highly dispersed as single molecules and so the influence of the intermolecular field due to molecules of the solvent is not large enough to cause a splitting of the energy level.

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Swamy (1953) studied the ultraviolet absorption spectra of ortho-and para-bromotoluene in the solid state at —180°C. In the case of ortho-bromotoluene each absorption band was found to be split up into three components, while in the case of para-bromotoluene no much splitting was observed. Recently, Sen (1956) studied ultraviolet absorption spectra of meta-bromotoluene both in the liquid and solid states at —180°C and observed splitting of the energy level as in the case of the ortho compound in the solid state.

In order to study how the environments affect the intermolecular field when these substances are dissolved in suitable solvents in various proportions and frozen and cooled to —180°C, an investigation of the ultraviolet absorption spectra of frozen solutions of ortho-, meta- and para bromotoluene in isobutyl alcohol of different concentrations was undertaken and the results which are discussed in the present paper support the conclusions drawn earlier (Roy, 1956) that the splitting of the energy level is due to formation of associated groups of the molecules in the solid state.

EXPERIMENTAL

The experimental arrangement in the present investigation was the same as that described in the previous paper (Roy, 1956). The bromotoluenes were of chemically pure quality. The purity of isobutyl alcohol used as solvent was tested by studying its absorption spectrum. All the liquids were distilled under reduced pressure before use. Solutions of two different concentrations were studied. In each case solutions of strength 0.2% and 40% were used. When the dilute solution was frozen it was transparent and homogeneous. In this case the absorption cell, described in the previous investigation (Roy 1956) was used. The 40% solution was translucent in the frozen state. In this case the absorption cell used was the same as that used by Swamy (1952), but the thickness was controlled by using aluminium foil of thickness of the order of .01 mm. A hydrogen discharge tube running at 3 KV served as the source of continuous spectrum. Spectrograms were taken on Ilford HP3 film. Microphotometric records of these spectrograms were taken with a Kipp and Zonen type self-recording microphotometer. Iron arc spectrum was recorded on each spectrogram as comparison. The frequencies of the absorption bands were measured with the help of these microphotometric records of the absorption spectra in which records of the two known iron lines were taken as reference lines, and the records of the iron arc spectrum.

RESULTS

The microphotometric records of the spectra are reproduced in figures 1, 2 and 3 and the wave numbers of the bands and their probable assignments are given in Tables I, II, III, IV, V and VI.

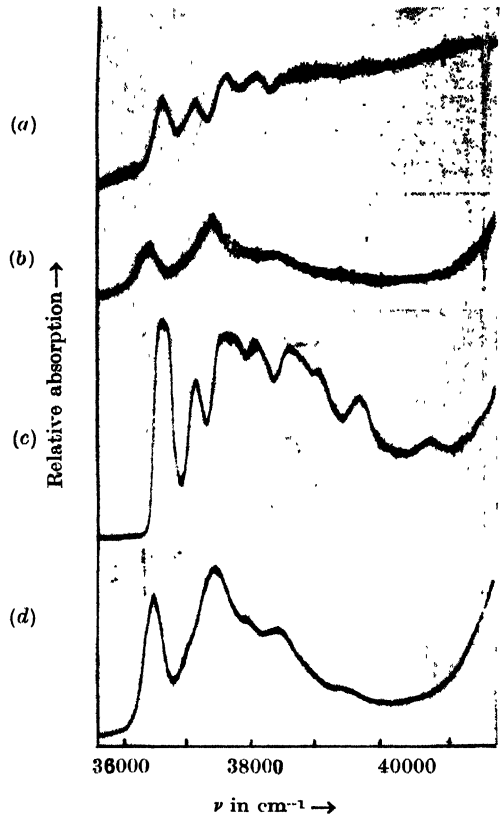

Fig. 1. Michophotometric records of the ultraviolet absorption spectra of solutions of *o*-bromotoluene in isobutyl alcohol.

(*a*) 40 % Frozen solution at — 180°C

(*b*) 40 % Solution at 30°C

(*c*) 0.2 % Frozen solution at — 180°C

(*d*) 0.2 % Solution at 30°C

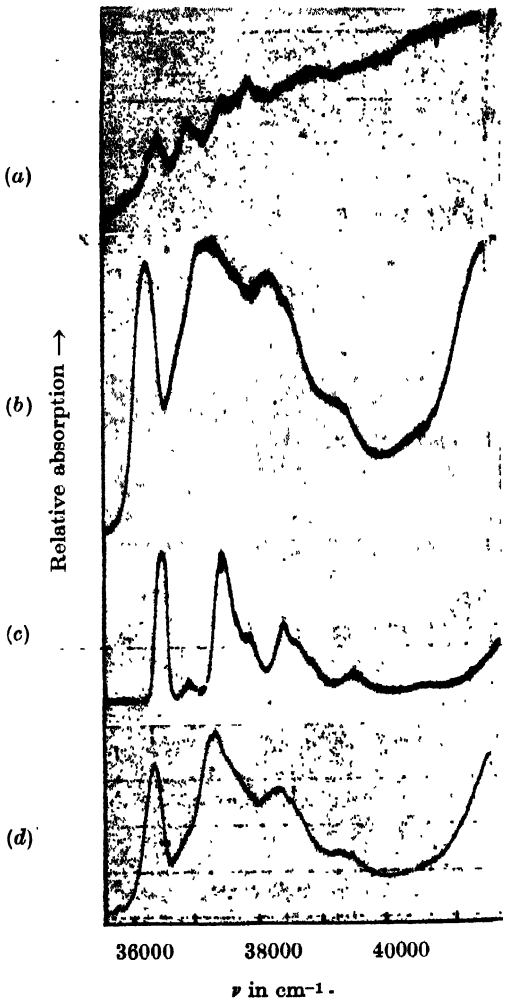

Fig. 2. Microphotometric records of the ultraviolet absorption spectra of solutions of *m*-bromotoluene in isobutyl alcohol.
(*a*) 40% Frozen solution at − 180°C.
(*b*) 40% Solution at 30°C
(*c*) 0.2% Frozen solution at − 180°C
(*d*) 0.2% Solution at 30°C.

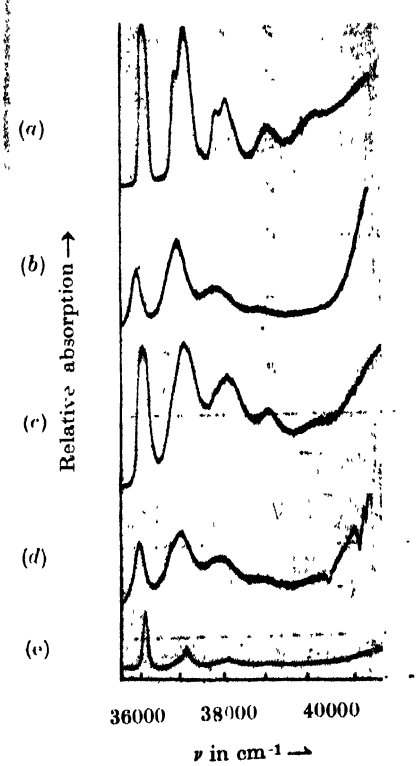

Fig. 3, Microphotometric records of ultraviolet absorption spectra of *p*-bromotoluene and its solution in isobutyl alcohol.
(a) 40% Solution at − 180°C
(b) 40% Solution at 30°C
(c) 0.2% Solution at − 180°C
(d) 0.2% Solution at 30°C
(e) *p*-Bromotoluene at − 180°C

TABLE I

Absorption spectra of *o*-bromotoluene

Vapour (Swamy, 1953)		Pure liquid (Swamy, 1553)		Soln. in isobutyl alcohol (Present author)			
				0.2%		40%	
ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment
		36450(Vs,b)	ν_0	36512 (s)	ν_0	36472 (s)	ν_3
36780	ν_0-74						
36854	ν_0			36998 (w)	ν_0+486		
37280	ν_0+426					37456 (s)	ν_3+984
37330	ν_0+476						
		37432(S,b)	ν_0+982	37512 (s)	ν_0+1000		
37825	ν_0+971						
37876	ν_0+1022						
38796	$\nu_0+2\times971$			37997 (m)	$\nu_0+486+1000$		
						38450 (m)	$\nu_3+2\times984$
38848	$\nu_0+971+1022$	38420 (w)	$\nu_0+2\times982$	38489 (m)	$\nu_0+2\times1000$		
38900	$\nu_0+2\times1022$						
				39480 (w)	$\nu_0+3\times1000$		

TABLE II

Absorption spectra of *o*-bromotoluene

Pure solid at −180°C (Swamy, 1953)		Frozen solution in isobutyl alcohol (Present author)			
		0.2%		40%	
ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment
		36646 (V,s)	ν_0	36646 (s,b)	ν_0
36730 (m)	C_0				
36950 (w)	B_0				
		37117 (m)	ν_0+471	37117 (s,b)	ν_0+471
37176 (s)	A_0				
		37641 (s)	ν_0+995	37641 (s,b)	ν_0+995
37690 (m)	C_1				
37912 (w)	B_1				
		38111 (s)	$\nu_0+471+995$	38111 (s,b)	$\nu_0+471+995$
38140 (s)	A_1				
		38635 (s)	$\nu_0+2\times995$	38635 (m,b)	$\nu_0+2\times995$
38655 (m)	C_2				
38880 (w)	B_2				
39104 (w) ±	A_2				
		39106 (m)	$\nu_0+471+2\times995$		
		39630 (m)	$\nu_0+3\times995$		
		40624 (w)	$\nu_0+4\times995$		

TABLE III

Absorption spectra of *m*-bromotoluene

Vapour (Sen, 1956)		Pure liquid (Sen, 1956)		Soln. in isobutyl alcohol (Present author)			
				0.2%		40%	
ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment
		36197 (s,b)	ν_0			36286 (s)	ν_0
36359 (s)	ν_0-167			36366 (s)	ν_0		
36526 (vs)	ν_0			36821 (w)	ν_0+455		
36987 (m)	ν_0+461					37246 (s)	ν_0+960
		37223 (s,b)	ν_0+1026	37330 (s)	ν_0+964		
37492 (s)	ν_0+966			37554 (m)	ν_0+1188		
37730 (m)	ν_0+1204	38247 (m,s,b)	$\nu_0+2\times 1026$	37781 (m)	$\nu_0+455+964$	38201 (m)	$\nu_0+2\times 960$
				38302 (m)	$\nu_0+2\times 964$		
		39277(w,b)	$\nu_0+3\times 1026$	39250 (w)	$\nu_0+3\times 964$	39160	$\nu_0+3\times 960$

TABLE IV

Absorption spectra of *m*-bromotoluene

Pure Solid (Sen, 1956)		Frozen soln. in isobutyl alcohol (Present author)			
		0.2%		40%	
ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment
36123 (m)	C_0	36485 (V,s)	ν_0	36485 (s,b)	ν_0
36570 (v,s)	A_0	36917 (v,w)	ν_0+432	36917 (s,b)	ν_0+432
37004 (s)	B_0				
37108 (m)	C_1	37456 (s)	ν_0+971	37456 (s,b)	ν_0+971
37554 (m)	A_1	37667 (m)	ν_0+1182	37667 (s,b)	$\nu_0+971+432$
		37882 (m)	$\nu_0+432+971$		
37992 (ms)	B_1				
38098 (w)	C_2	38420 (m)	$\nu_0+2\times 971$	38420 (m,b)	$\nu_0+2\times 971$
38541 (w)	A_2	38613 (m)	$\nu_0+971+1182$		
38982 (ms)	B_2	38851 (w)	$\nu_0+2\times 971+432$		
		39404 (w)	$\nu_0+3\times 971$		
		40361 (w)	$\nu_0+4\times 971$		

TABLE V

Absorption spectra of *p*-bromotoluene

Vapour (Swamy, 1953)		Pure liquid (Swamy, 1953)		Solution in isobutyl alcohol (Present author)			
				0.2%		40%	
ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment
		35803 (vs,b)	ν_0				
				35986 (s)	ν_0	35947 (s)	ν_0
36173	ν_0						
				36754 (m)	ν_0+768		
		36827 (s)	ν_0+1025				
36928	ν_0+755					36957 (s)	ν_0+1010
				36998 (s)	ν_0+1012		
37189	ν_0+1016						
				37767 (m)	ν_0+768 $+1012$		
		37849 (w)	ν_0+ 2×1025			37968(m)	ν_0+ 2×1010
37954	ν_0+755 $+1016$						
				38011 (m)	$\nu_0+2\times1012$		
38205	ν_0+ 2×1016						
						38989 (w)	ν_0+ 3×1010
				39020 (w)	$\nu_0+3\times1012$		

TABLE VI

Absorption spectra of *p*-bromotoluene

Pure solid Present author		Frozen solution in isobutyl alcohol (Present author)			
		0.2%		40%	
ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment
		36064 (s)	ν_0		
36129 (vs)	ν_0			36129 (v.s)	ν_0
		36852 (m)	ν_0+788		
36903 (m)	ν_0+774			36903 (m)	ν_0+774
		37081 (s)	ν_0+1016		
37150 (s)	ν_0+1021			37150 (s)	ν_0+1021
		37871 (m)	$\nu_0+788+1016$		
37925 (w)	$\nu_0+774+1021$			37925 (w)	$\nu_0+1021+774$
		38083 (m)	$\nu_0+2\times1016$		
38154 (m)	$\nu_0+2\times1021$			38156 (m)	$\nu_0+2\times1021$
		39096 (w)	$\nu_0+3\times1016$		
				39176 (w)	$\nu_0+3\times1021$
		40116 (w)	$\nu_0+4\times1016$		
				40200 (w)	$\nu_0+4\times1021$

DISCUSSION

o-Bromotoluene

It can be seen from Tables I and II that in the case of 0.2% solution of *o*-bromotoluene in isobutyl alcohol in the liquid state, the position of the 0,0 band is shifted towards shorter wavelengths from the position of the 0,0 band due to

pure liquid by 60 cm^{-1} and from its position in the vapour state by 342 cm^{-1} towards longer wavelengths. Thus the influence of the solvent molecules is a little smaller than that due to the molecules of the pure substance. When this solution is frozen the 0,0 band shifts by 130 cm^{-1} towards shorter wavelengths. On comparing the absorption spectrum of 0.2% frozen solution of *o*-bromotoluene with that due to the pure substance in the solid state as reported by Swamy (1953), it is found that the splitting of the band system into three systems observed in the case of the crystals of the pure substance does not take place in the case of 0.2% solution in the solid state. But the 0,0 band due to the frozen solution is shifted by about 208 cm^{-1} towards longer wavelengths with respect to the 0,0 band due to the vapour state. This shift of the 0,0 band shows that in the solid state the alcohol molecules surrounding the *o*-bromotoluene molecules exert a strong influence on the electronic energy level of the molecule, but the energy level is split up into three components only when the *o*-bromotoluene molecules are surrounded by the same molecules. The absorption spectrum due to a 40% solution of *o*-bromotoluene in the solid state shows that in this spectrum, the band system due to the pure substance in the solid state is superposed on that due to 0.2% solution in the frozen state. These results could be interpreted by assuming that the splitting of the bands is caused by the lattice field in the crystals of the pure substance and as the molecules are dispersed in the 0.2% frozen solution the lattice is absent and the splitting does not occur. If the above assumption were correct, it would be necessary to conclude that in 40% solution at −180°C some crystallites of the pure substance are present. Attempts were made to find out whether small crystals of *o*-bromotoluene separate out when the 40% solution is cooled. It was found, however, that the whole mixture freezes almost simultaneously and the frozen mass appears to be opaque. This shows that the molecules of *o*-bromotoluene are mixed up with those of the alcohol in the solid state. Probably most of them remain in small groups of associated molecules in the 40% frozen solution and as single molecules in 0.2% solution, so that the latter appears to be quite transparent while the former is opaque owing to the difference in the refractive indices of the groups of *o*-bromotoluene molecules. Hence it is to be concluded that the splitting of the energy level is due to the formation of such groups in 40% solution at −180°C and in the pure crystals of *o*-bromotoluene.

m-Bromotoluene.

It can be seen from Tables III and IV that in the case of 0.2% and 40% solution of *m*-bromotoluene in isobutyl alcohol in the liquid state the 0,0 band is displaced by about 160 cm^{-1} and 240 cm^{-1} respectively towards longer wavelengths with respect to its position in the spectrum due to the vapour phase. This shift in the case of the pure liquid is about 323 cm^{-1}. In the case of 0.2% solution the bands can be assigned to progressions of excited state frequencies 455, 964 and 1188 cm^{-1} as in the case of the vapour, but the spectrum due to 40%

solution in the liquid state resembles that due to the pure liquid with the difference that the excited state frequency 1026 cm^{-1} in the liquid state diminishes to 966 cm^{-1} in the case of 40% solution. When the solutions are frozen and cooled to −180°C, the 0,0 band due to 0.2% solution shifts further towards its position in the vapour state while that due to 40% solution seems to be a broad band composed of the 0,0 band due to the frozen 0.2% solution and that due to the pure crystal. In this case also the molecules are probably present in small groups as in the case of ortho compound.

p-Bromotoluene.

It can be seen from Tables V an VI that the absorption spectra of 0.2% solution of *p*-bromotoluene in isobutyl alcohol can be assigned to progressions of two excited state frequencies 768 cm^{-1} and 1012 cm^{-1} as in the case of the vapour. The absorption spectra due to 40% solution is almost similar to that due to pure liquid, the bands due to the progressions of excited state frequencies 755 cm^{-1} being absent. The displacement of the band system with the changes of state observed in this case is much smaller than that in the case of the ortho-or meta compound. Also the spectrum due to the pure crystals does not indicate any splitting of the bands observed in the case of the other two isomers. If the splitting would be due to the lattice field, it would take place in this case also. So the absence of any splitting in this case indicates that the splitting is not due to lattice field, but it is due to presence of strongly asymmetric groups of molecules in the crystal. Probably, owing to the small value of dipole moment in the *p*-bromotoluene molecule, the molecules do not form large groups of associated molecules. The small shift of the 0,0 band with liquefaction of the vapour, however, indicates that the intermolecular field has a small influence on the position of 0,0 band and this may be due to the formation of small symmetric groups. In the solid state the regular distribution of such groups around any molecule may diminish the resultant intermolecular field acting on the molecule.

Investigations with other liquids are in progress.

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